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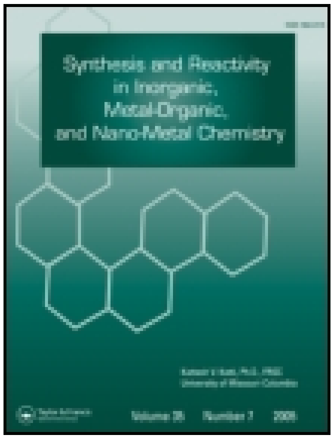

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Synthesis and Spectroscopic Characterization of Zr(IV) and Th(IV) With Chelating Containing ONNO Donor Quadridentate Schiff Bases Complexes

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Synthesis and Spectroscopic Characterization of Zr(IV) and Th(IV) With Chelating Containing ONNO Donor Quadridentate Schiff Bases Complexes

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New metal complexes of novel Schiff bases derived from the reaction of zirconium (IV) and thorium (IV) ions with *N*,*N*′-disalicylidene-l,2-phenylenediamine (H_2dsp), *N*,*N*′-disalicylidene-3,4-diaminotoluene (H_2dst), 4-nitro-*N*,*N*-disalicylidene-1,2-phenylenediamine (H_2ndsp) were prepared and characterized based on elemental analyses, IR and ^{1}H NMR spectroscopy, molar conductance, and thermal analyses. The complexes are formed in 1:1 [Metal]:[Ligand] ratio. The molar conductance measurements proved that all these complexes are non-electrolytes. The IR spectra of the ligands and their complexes are used to identify the type of bonding. The thermogravimetric analysis of the complexes shows metal oxide remaining as the final product.

Keywords: Schiff base, zirconium (IV), thorium (IV)

Introduction

Schiff bases are compounds containing an azomethine group (−C=N−) have drawn attention for many years ago. They are capable of forming coordinate bonds with many metal ions through both azomethine group and phenolic group or via its azomethine or phenolic group.[1–3] Their metal complexes have been studied, with a variety of transition metal ions, as they frequently exhibit unusual structural properties. These properties have resulted in wide applications in the biological field including antitumor, antibacterial, fungicidal, and anticarcinogenic properties.[4–6] Some Schiff base complexes are also used as model molecules for biological oxygen carrier systems as well as having applications in analytical fields.[7,8] The most important step in the development of metal complexes was perhaps the preparation of a new ligand, which exhibit unique properties and novel reactivity. Because of the electron donor and electron acceptor properties of the ligand, structural functional groups and the position of the ligand in the coordination sphere together with the reactivity of coordination compounds may be a factor of different studies.[9–14] In continuation of our ongoing research on the development of new Schiff base complexes derived from *N*,*N*′-bridged tetradentate ligands involving an N_2O_2 donor atoms[2]; herein, we study the reaction of *N*,*N*′-disalicylidene-l,2-phenylenediamine (H_2dsp), *N*,*N*′-disalicylidene-3,4-diaminotoluene (H_2dst), 4-nitro-*N*,*N*′-disalicylidene-1,2-phenylene-diamine (H_2ndsp) with Zr(IV) and Th(IV) ions. The products were characterized. The products were structurally characterized using elemental analysis, infrared (IR), and ^{1}H NMR. Finally, the thermal behavior of the obtained complexes was also investigated.

Experimental

Chemicals and Instruments

All of the chemicals used were of high reagent grade and were used without further purification. Zr(IV) sulfate and Th(IV) nitrate were purchased from the BDH Chemical Company and were used without further purification. Carbon, hydrogen and nitrogen content were determined using a Perkin Elmer CHN 2400 in the Microanalytical Unit at the Faculty of Science, Cairo University, Egypt. The metal content was found gravimetrically by converting the compounds into their corresponding oxide. IR spectra were recorded on Bruker FT-IR spectrophotometer (400–400 cm^{-1}) in KBr pellets. Molar conductivities of freshly prepared 1.0 × 10^{-3} mol dm^{-3} DMSO solutions were measured using Jenway 4010 conductivity meter. ^{1}H-NMR spectra were recorded on Varian Gemini 200 MHz spectrometer using DMSO-d_6 as solvent and TMS as an internal reference. Thermogravimetric analysis (TGA and DTG) was carried out in dynamic

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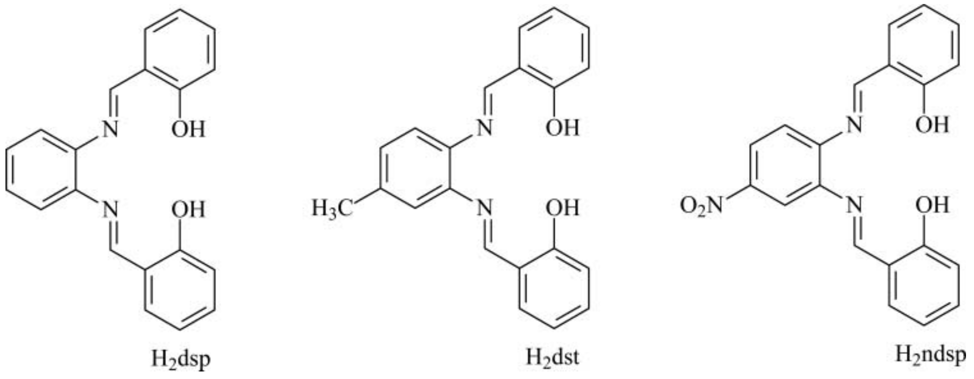

H_2dsp H_2dst H_2ndsp

Sch. 1. Chemical Structure of the H_2dsp, H_2dst and H_2ndsp ligands.

nitrogen atmosphere (30 mL/min) with a heating rate of 10°C/min. using Shimadzu TGA-50H thermal analyzer.

Procedures

Synthesis of the ligands

The H_2dsp, H_2dst, and H_2ndsp ligands (Scheme 1) were prepared by Garg and Kumar method.[15,16] All the tetradentate Schiff base ligands except H_2dst were prepared by condensations between diamines and hydroxyaldehydes in ethanol or methanol and were purified by recrystallization from a dichloromethane/hexane mixed solvent through the partial evaporation of the more volatile dichloromethane. The H_2dst ligand was prepared by dissolving 25 mmol (3.050 g) of 3,4-diaminotoluene in 100 mL of ethanol and stirred for 3 h. After that, 50 mmol (6.106 mL) of salicylaldehyde was mixed in 150 mL of ethanol. The 3,4-diaminotoluene solution was added to the salicylaldehyde solution using an overhead stirred for complete mixing. Some yellow precipitate resulted. The crude product was re-crystallized from dichloromethane/hexane (1:2) mixed solvent.

Table 1. Elemental analysis and physical data of the complexes

		Content: (Calcd.) Found (%)				
Compound	M (wt%)	C	H	N	Metal	Λ_m (Ω^{-1} cm^{-1} mol^{-1})
$[Zr(dsp)(SO_4)(H_2O)].2H_2O$	555.22	(43.23) 43.29	(2.5) 2.6	(5.04) 5.0	(16.43) 16.40	17.40
$[Th(dsp)(NO_3)_2].H_2O$	688.0	(34.88) 34.81	(2.33) 2.29	(8.14) 8.17	(33.72) 33.75	20.50
$[Zr(dst)(SO_4)(H_2O)].4H_2O$	605.22	(41.64) 41.60	(4.30) 4.33	(4.63) 4.65	(15.07) 15.0	18.70
$[Th(dst)(NO_3)_2].H_2O$	702.0	(35.9) 35.77	(2.56) 2.61	(7.98) 7.97	(33.05) 33.1	20.40
$[Th(ndsp)(NO_3)_2].H_2O$	733.0	(32.74) 32.72	(2.05) 2.03	(9.55) 9.51	(31.65) 31.68	60.40

Synthesis of the metal complexes

One mmol of each metal salt; Zr(IV) or Th(IV) was dissolved in methanol, and 1 mmol of requisite ligand was suspended in hot methanol and stirred for 1 h. The methanolic solutions

Table 2. IR frequencies (cm^{-1}) of the free ligands and their complexes

	Assignment						
Compound	ν_{as}(OH) H_2O	ν(O—H)	ν(C=N)	ν(C—N)	ν(ph-O)	ν(M—N)	ν(M—O)
H_2dsp	—	2500–2680	1614	1403	1325	—	—
H_2dst	—	2550–2750	1617	1401	1350	—	—
H_2ndsp	—	2650–2750	1635	1372	1313	—	—
$[Zr(dsp)(SO_4)(H_2O)].2H_2O$	3400	—	1615	1464	1307	530	444
$[Th(dsp)(NO_3)_2].H_2O$	3390	—	1617	1380	1304	538	467
$[Zr(dst)(SO_4)(H_2O)].4H_2O$	3430	—	1630	1420	1320	530	436
$[Th(dst)(NO_3)_2].H_2O$	3400	—	1610	1383	1302	585	467
$[Th(ndsp)(NO_3)_2].H_2O$	3420	-	1627	1447	1379	473	409

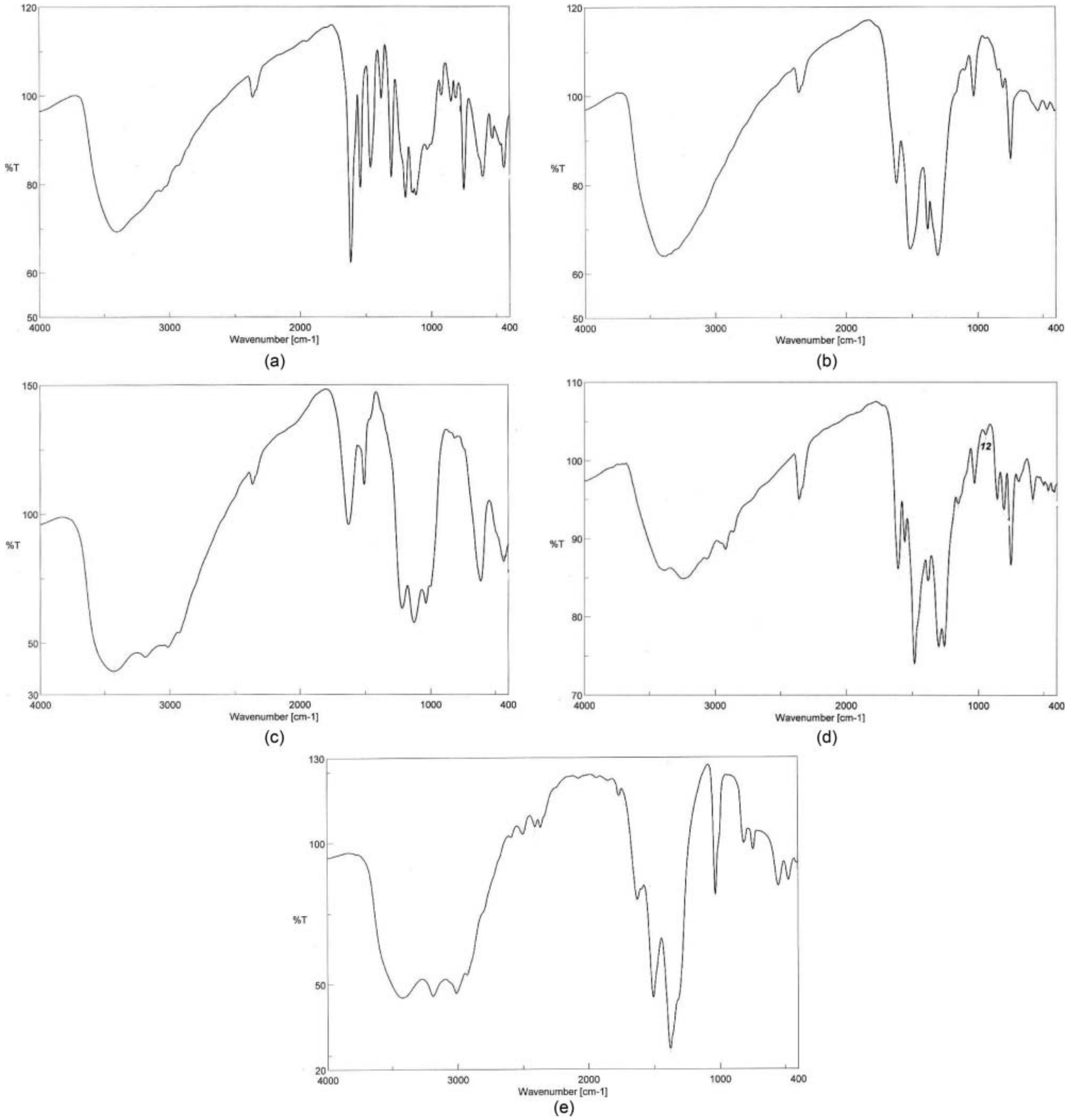


Fig. 1. **(a)** IR spectrum of [Zr(dsp)(SO_4)(H_2O)].2H_2O complex. **(b)** IR spectrum of [Th(dsp)(NO_3)$_2$].H_2O complex. **(c)** IR spectrum of [Zr(dst)(SO_4)(H_2O)].4H_2O complex. **(d)** IR spectrum of [Th(dst)(NO_3)$_2$].H_2O complex. **(e)** IR spectrum of [Th(ndsp)(NO_3)$_2$].H_2O complex.

Table 3. ^{1}H NMR spectral data[a] (δ, ppm)[b] of the free H_2dsp ligand and [Zr(dsp)(SO_4)(H_2O)].2H_2O

Compound	(OH) phenolic	N = CH	Aromatic protons
H_2dsp	12.95	8.58	7.1–7.4, 6.8–7.03
H_2dst	13.14, 13.08	8.58, 8.57	7.26–7.36, 6.94–7.11, 6.70–6.90
H_2ndsp	12.52, 12.45	8.73, 8.65	8.14–8.24, 7.30–7.46, 6.90–7.08
[Zr(dsp)(SO_4)(H_2O)].2H_2O	—	8.72	7.6–7.0, 6.97–6.4

[a] Solvent DMSO-d_6.

[b] Relative to TMS.

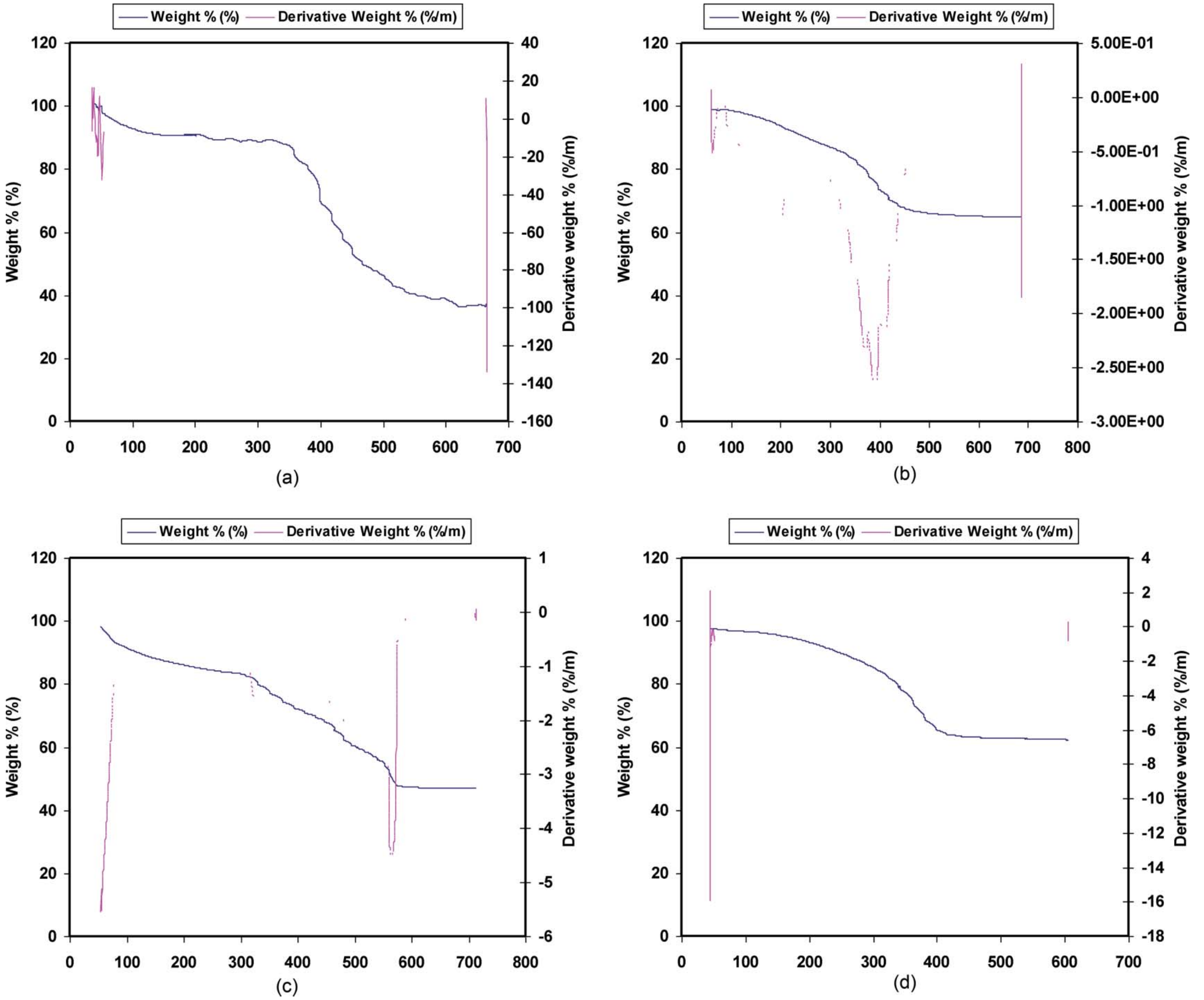


Fig. 2. (a) The TGA and DTG of [Zr(dsp)(SO_4)(H_2O)].2H_2O complex. **(b)** The TGA and DTG of [Th(dsp)(NO_3)$_2$].H_2O complex. **(c)** The TGA and DTG of [Zr(dst)(SO_4)(H_2O)].4H_2O complex. **(d)** The TGA and DTG of [Th(dst)(NO_3)$_2$].H_2O complex.

of the metal ion were added to methanolic Schiff base solutions and the resulting mixtures were refluxed for 3 h and evaporate to half. After cooling, the microcrystalline solids were filtered off, washed with hot methanol, and dried at 60°C.

Results and Discussion

Elemental Analysis Results

The elemental analysis (C, H, and N) results and some physical characteristics of the obtained complexes are shown in Table 1. The results indicate that all complexes are formed in 1:1 [Metal]:[Ligand] ratio. The complexes are air-stable, hygroscopic, with higher melting points (>300°C), insoluble in H_2O and most of organic solvents except for DMSO and DMF.

Molar Conductance Measurements

Conductivity measurements have frequently been used in structural studies of metal chelates within the limits of their solubility. They provide a method of testing the degree of ionization of the complexes, the molar ions that a complex liberates in solution, the higher will be its molar conductivity and vice versa.[17] The molar conductivities of 1.0×10^{-3} mol dm^{-3} solutions (DMSO solvent) of the free ligands and their complexes are measured and the data obtained are listed in Table 1. The molar conductance values of the free ligands were in the range 4.46–6.90 Ω^{-1} cm^{-1} mol^{-1}, while those of

Table 4. Thermal decomposition data for the complexes

Complex	T_{max} (°C)	% Weight loss Calcd.	% Weight loss Found	Assignment
$[Zr(dsp)(SO_4)(H_2O)].2H_2O$	180	9.7	9.4	$3H_2O$
	400	52.9	52.9	$C_{13}H_{14}N_2O_4S$
	—	37.0	37.1	$ZrO_2 + 7C$ residue
$[Th(dsp)(NO_3)_2].H_2O$	200	11.6	11.59	$H_2O + NO_2$
	390	22.1	22.5	$C_4H_{14}N_3O_4$
	—	66.3	66.2	$ThO_2 + 16C$ residue
$[Zr(dst)(SO_4)(H_2O)].4H_2O$	200	14.1	14.48	$5H_2O$
	477	23.8	23.5	$C_3H_6NO_2 + SO_2$
	560	11.36	12.0	$C_3H_8N_2$
	—	50.44	49.72	$ZrO_2 + 16C$ residue
$[Th(dst)(NO_3)_2].H_2O$	300	2.5	1.8	H_2O
	590	32.6	33.0	$C_5H_{17}N_4O_6$
	—	64.8	65.0	$ThO_2 + 16C$ residue
$[Th(ndsp)(NO_3)_2].H_2O$	180	8.7	8.72	$H_2O + NO_2$
	240	44.0	45.7	$C_{13}H_{14}N_2O_6$
	—	47.4	47.3	$ThO_2 + 7C$ residue

the complexes were in the range 15–60 Ω^{-1} cm^{-1} mol^{-1}. It is concluded from these results that that the complexes are considered as non-electrolytes. These low molar conductance values indicate their nonionic nature. The higher values of the complexes than that of the corresponding ligands indicate the formation of complexes and the presence of sulfate or nitrate ion.

Infrared Spectra

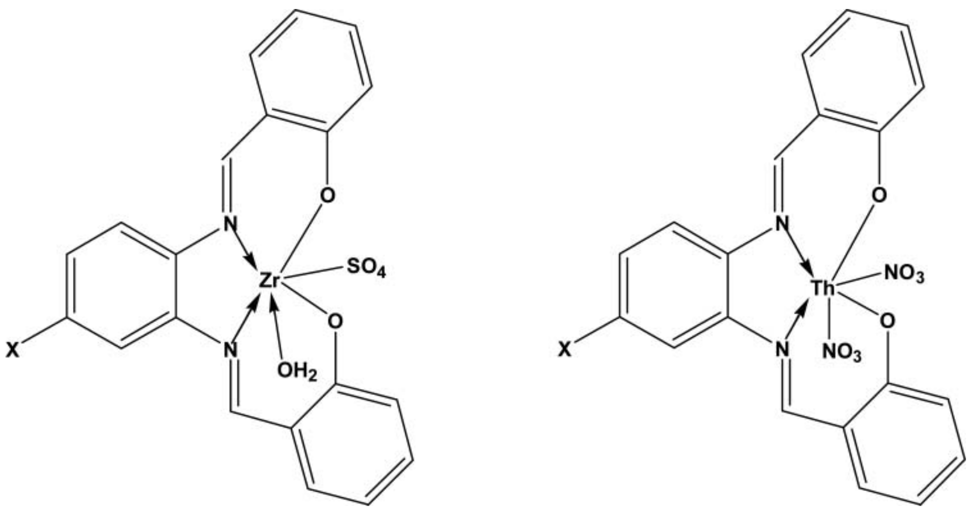
The infrared absorption spectra of the free ligand and their complexes were recorded in the frequency range 4000–400 cm^{-1} using a KBr disc, and their characteristic bands are provided in Table 2. The full IR spectra of the obtained complexes are shown in Figure 1a–e. All the complexes containing water molecules, so they exhibited characteristic medium intensity absorption bands in the region 3200–3500 cm^{-1}.[18] The spectra of the ligands exhibited broad medium intensity bands in the 2500–3360 cm^{-1} range that are attributed to the intramolecular H-bonding vibration (O—H···N), while in the spectra of the complexes these bands were disappeared. The vibrations of the azomethine groups of the free ligands were observed at the range (1610–1640 cm^{-1}). These bands were shifted to higher frequencies in the complexes, indicating that the nitrogen atom of the azomethine group is coordinated to the metal ion.[2,19] In the ligands spectra, the bands observed at the range of 1311–1350 cm^{-1}, which can be assigned to the phenolic (C—O) group vibrations,[19] were shifted toward higher or lower frequency in the complexes spectra, indicating chelation of oxygen to the metal ions. In all the complexes, the bands at 473–585 and 409–467 cm^{-1} range can be attributed to the ν(M-N) and ν(M-O) modes, respectively.

^{1}H NMR Spectra

The nuclear magnetic resonance spectra provide evidence of the complexation pathway. The 400 MHz ^{1}H NMR spectra of the free H_2dsp ligand and its complex with Zr(IV) were measured in DMSO-d_6 at room temperature. The chemical shift (δ, ppm) of the different protons has been recorded in Table 3. The ^{1}H NMR spectrum of all the Schiff bases provides completing evidence of the presence of either one or two azomethine groups. Due to different chemical environments two signals are recorded for the azomethine protons in the H_2dst and H_2ndsp ligands, whereas, the H_2dsp ligand gives one signal. By comparing the ^{1}H NMR spectra of H_2dsp ligand and $[Zr(H_2dsp)(SO_4)(H_2O)].2H_2O$ complex, it is noted that there is a downfield sift in the frequency of azomethine protons of aromatic bridge and upfield shift in the aliphatic bridge confirming coordination of the metal ion to both groups. In the complex, no signal is recorded for phenolic hydrogen in the 12–13.5 ppm region, as in the case of the Schiff base indicating deprotonation of the orthohydroxyl group.

Thermal Analyses

To determine the formula and structure of the new complexes, thermogravimetric analysis (TG and DTG) was performed for these complexes over a temperature range of 25–700°C under a static air atmosphere. The TG curves were redrawn with the mg mass loss as a function of temperature. Figure 2 shows the thermograms for the complexes, whereas Table 4 provides the thermal analysis data of these complexes. The obtained data strongly support the structures proposed for the complexes. The thermal decomposition of $[Zr(dsp)(SO_4)(H_2O)].2H_2O$ complex occurs at two steps. The first degradation step take place in the range of 50–



Sch. 2. Proposed structures of H_2dsp, H_2dst and H_2ndsp complexes (where x = H, CH_3 or NO_2).

180°C and it is corresponds to the elimination of three water molecules due to a weight loss of 9.7% in a good matching with theoretical value 9.4%. The second step fall in the range of 180–380°C, which is assigned to loss of C13H14N2O4S with a weight loss 52.91%, and the calculated value is 52.92%. The ZrO_2 (Figure 3) is the final product remains stable until 700°C with few carbon atoms. The thermal decomposition of [Th(dsp)$(NO_3)_2$].H_2O complex completely occurs in two steps. The first step ranged at 50–200°C corresponding to the loss of NO_2 and H_2O molecules, representing a weight loss of 11.59% and its calculated value is 11.6%. The second step ranged at 200–400°C corresponding to the loss of $C_4H_{14}N_3O_4$, representing a weight loss of 22.50% and its calculated value is 22.1%. The ThO_2 (Figure 3) is the final product remains stable until 700°C with few carbon atoms. The [Zr(dst)$(SO_4)(H_2O)$].$4H_2O$ complex decomposed in three steps. The first step extended from 50 to 200°C and can be assigned to the loss of $5H_2O$ molecules, representing a weight loss of 14.2% and its calculated value is 15%. The second step occurring at 326–477°C corresponding to the loss of $C_3H_6NO_2$ and SO_2, representing a weight loss of 23.5% and its calculated value is 23.8%. The final step occurring at 477–560°C, corresponding to loss of $C_3H_8N_2$ (organic moiety), representing a weight loss of 12% and its calculated value is 11.36%. The final products resulted at 700°C contain ZrO_2 polluted with some carbon atoms. The thermal decomposition of [Th(dst)$(NO_3)_2$].H_2O complex proceeds approximately with main two degradation step. The weight loss associated with the first stage is 1.8% and its calculated value is 2.5%, corresponding to the loss of one H_2O molecule. The weight loss associated with the second stage is 33% and its calculated value is 32.6%, corresponding to the loss of $C_5H_{17}N_4O_6$. The final product results at 700°C contains of ThO_2 with a few carbon atoms. The [Th(ndsp)$(NO_3)_2$].H_2O complex decomposed in two steps. The weight loss associated with the first stage is 8.72%, which is very close to the theoretical value of 8.70, corresponding to the loss of $H_2O + NO_2$ molecules. The second stage representing a weight loss of 45.7% and its calculated value is 44%, corresponding to the loss of $C_{13}H_{14}N_2O_6$ (organic moiety). The final product resulted at 700°C contains of ThO_2 polluted with a few carbon atoms. The reported data dealing in the thermal analysis within nitrogen atmosphere indicate that the complexes decompose to give metal oxide contaminated with carbon atoms as final products. This reason, because of no sufficiently of oxygen atoms help to evolved carbon as carbon monoxide or dioxide.

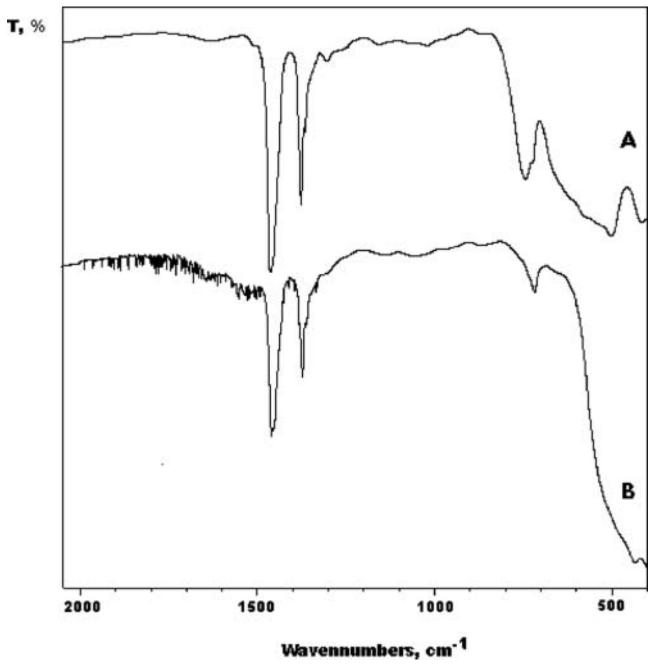


Fig. 3. Infrared spectra of the final residual of thermal decomposition for (A) zirconium(IV) and (B) thorium(IV) complexes.

Structure of the Complexes

The structures of the obtained complexes are confirmed by elemental analysis, molar conductance, IR and ^{1}H NMR spectra, and thermal analysis. The proposed structures of these complexes are shown in Scheme 2.

Conclusion

Structural studies of new Zr(IV) and Th(IV) complexes with three Schiff bases (H_2dsp, H_2dst, and H_2ndsp) were carried out. It is observed that the reaction stoichiometry is 1:1 [Metal]:[Ligand] ratio. The IR and ^{1}H NMR spectra show that the Schiff bases acted as dianionic tridentate N_2O_2 donors attached to the metal acceptor centre through the deprotonated two phenolic oxygen groups and two azomethine nitrogen groups. The proposed structure of the resulted complexes is six-coordinated fashion.

References

1. Sadeek, S. A.; Refat, M. S. *J. Korean Chem. Soc.* **2006**, *50*, 107.
2. Refat, M. S.; El-Korashy, S. A.; Kumar, D. N.; Ahmed, A. S. *Spectrochim. Acta A* **2008**, *70*, 898.
3. Hassan, W. M. I.; Zayed, E. M.; Elkholy, A. K.; Moustafa, H. Mohamed, G. G. *Spectrochim. Acta A* **2013**, *103*, 378.
4. Garnovskii, A. D.; Vasil Chenko, I. S. *Russ. Chem. Rev.* **2002**, *71*, 943.
5. Ren, S.; Wang, R.; Komatsu, K.; Bonoz-Krause, P.; Zyrianov, Y.; McKenna, C. E. *J. Med. Chem.* **2002**, *45*, 410.
6. Raman, N.; Thangaraja, A.; Kulandaisamy, C. *Trans. Met. Chem.* **2003**, *28*, 29.
7. Halve, A.; Samadhiya, S. *Orient. J. Chem.* **2001**, *17*, 87.
8. Weber, O. A.; Robinson, T. W.; Simeon, V. I. *J. Inorg. Nucl. Chem.* **1971**, *33*, 2097.
9. Tverdova, N. V.; Pelevina, E. D.; Giricheva, N. I.; Girichev, G. V.; Kuzmina, N. P.; Kotova, O. V. *J. Mol. Struct.* **2012**, *1012*, 151.
10. Anitha, C.; Sheela, C. D.; Tharmaraj, P.; Sumathi, S. *Spectrochim. Acta A* **2012**, *96*, 493.
11. Halli, M. B.; Sumathi, R. B.; Kinni, M. *Spectrochim. Acta A* **2012**, *99*, 46.
12. Sobha, S.; Mahalakshmi, R.; Raman, N. *Spectrochim. Acta A* **2012**, *92*, 175.
13. Abou-Hussein, A. A. A.; Linert, W. *Spectrochim. Acta A* **2012**, *95*, 596.
14. Singh, B. K.; Rajour, H. K.; Prakash, A. *Spectrochim. Acta A* **2012**, *94*, 143.
15. Garg, B. S.; Kumar, D. N. *Spectrochim. Acta* **2003**, *59A*, 229.
16. Kumar, D. N.; Garg, B. S. *Spectrochim. Acta* **2006**, *64*, 141.
17. Refat, M. S. *J. Mol. Struct.* **2007**, *742*, 24.
18. Jeewoth, T.; Bhowon, M. G.; Wah, H. L. K. *Trans. Met. Chem.* **1999**, *24*, 445.
19. Turner, M.; Celik, C.; Koksal, H.; Serin, S. *Trans. Met. Chem.* **1999**, *24*, 525.